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Reactions of the alkyltrihydroaluminate $\mathrm{[Li(thf)_2\{AlH_3[C(SiMe_3)_3]\}]_2}$. Crystal structures of $\mathrm{[Li(tmen)_2][AlH_3\{C(SiMe_3)_3\}]}$, $\mathrm{[AlBr_2\{C(SiMe_3)_3\}]{\cdot}thf}$, $\mathrm{[AlI_2\{C(SiMe_3)_3\}]{\cdot}thf}$, $\mathrm{[Li(thf)_2(\mu\text{-}NHPh)_2\{AlH[C(SiMe_3)_3]\}]}$ and $\mathrm{[Li(thf)_4][Al(NHPh)_3\{C(SiMe_3)_3\}]}$

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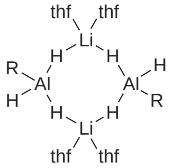
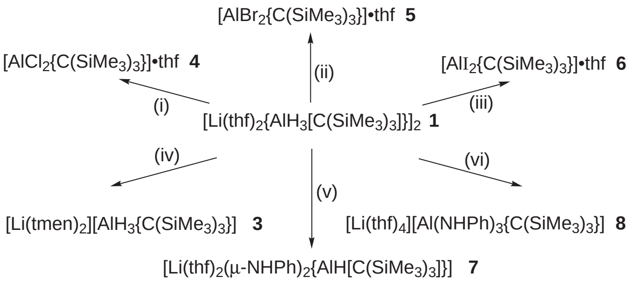
The alkyltrihydroaluminate $\mathrm{[Li(thf)_2\{AlH_3[C(SiMe_3)_3]\}]_2}$ (thf = tetrahydrofuran) reacted (i) with tetramethylethane-1,2-diamine (tmen) to give $\mathrm{[Li(tmen)_2][AlH_3\{C(SiMe_3)_3\}]}$, which crystallises as solvent-separated ion pairs, (ii) with HCl, HBr or $\mathrm{Br_2}$, or $\mathrm{I_2}$ to give, respectively, the alkylaluminium dihalides $\mathrm{[AlX_2\{C(SiMe_3)_3\}]{\cdot}thf}$, X = Cl, Br or I, which have been characterised spectroscopically and, when X = Br or I, by X-ray diffraction studies; and (iii) with aniline to give $\mathrm{[Li(thf)_2(\mu\text{-}NHPh)_2\{AlH[C(SiMe_3)_3]\}]}$ and $\mathrm{[Li(thf)_4][Al(NHPh)_3\{C(SiMe_3)_3\}]}$, which crystallise as anilido-bridged and solvent-separated ion pairs respectively.

We have previously[1,2] described the preparation and structures of the alkyltrihydroaluminates $\mathrm{[Li(thf)_2(AlH_3R)]_2}$, R = $\mathrm{C(SiMe_3)_3}$ **1** or $\mathrm{C(SiMe_2Ph)_3}$ **2**, thf = tetrahydrofuran, and the conversion of **1** into a series of lithium trifluoro-,[3] trialkoxo-[3,4] and tri(alkanethiolato)-alkylaluminates,[2] $\mathrm{Li[AlX_3\{C(SiMe_3)_3\}]{\cdot}}n\mathrm{thf}$ (X = F, $\mathrm{OPr^i}$, $\mathrm{OBu^t}$, $\mathrm{OCH_2Ph}$, $\mathrm{OCH_2Bu^t}$, or $\mathrm{OCHPh_2}$, $n = 1$; X = OMe, $n = 1$ or 4; X = OEt, OPh, SMe, SEt or $\mathrm{SPr^i}$, $n = 2$). Reactions of compound **1** with $\mathrm{Br_2}$, $\mathrm{I_2}$, HCl or HBr led to removal of the lithium and formation of alkylaluminium dihalides.[1,2] Similar reactions have been reported for aryltrihydroaluminates, *e.g.* those with R = 2,4,6-$\mathrm{R'_3C_6H_2}$ (R′ = $\mathrm{Pr^i}$, $\mathrm{Bu^t}$ or Ph) or 2,6-(2,4,6-$\mathrm{R''_3C_6H_2)_2C_6H_3}$, R″ = Me or $\mathrm{Pr^i}$;[5,6] with MeI or $\mathrm{SiMe_3Cl}$ gave the compounds $\mathrm{(RAlH_2)_2}$, $\mathrm{H_2RAl{\cdot}thf}$ or $\mathrm{Cl_2RAl{\cdot}thf}$.[6,7] Aluminate complexes $\mathrm{Li[AlCl_3R]}$ have been isolated[6,8] but they were obtained from reactions between organolithium compounds LiR and $\mathrm{AlCl_3}$.

Crystals of compound **2**, obtained from toluene, were shown to consist of hydrogen-bridged dimers comprising two $\mathrm{[Li(thf)_2]^+}$ cations and two $\mathrm{[AlH_3R]^-}$ anions; crystals of **1** were unsuitable for an X-ray diffraction study but the compound was shown to be dimeric in benzene by cryoscopic measurements.[1] In order to obtain crystallographic information on the structure of the $\mathrm{[AlH_3\{C(SiMe_3)_3\}]^-}$ anion we have examined the effect of replacing the thf in **1** by tetramethylethane-1,2-diamine (tmen) and in this paper we show that the crystals obtained from toluene consist of the compound $\mathrm{[Li(tmen)_2][AlH_3\{C(SiMe_3)_3\}]}$ **3**, containing discrete cations and anions. We also describe the reactions of **1** with HCl, HBr or $\mathrm{Br_2}$, or $\mathrm{I_2}$ to give, respectively, the thf complexes of the alkylaluminium dihalides $\mathrm{[AlX_2\{C(SiMe_3)_3\}]{\cdot}thf}$ (X = Cl **4**, Br **5** or I **6**), mentioned only briefly in previous publications.[1,2] Reactions with aniline, like those with HF, alcohols or thiols, give compounds containing lithium, *viz.* the alkylbis(amido)hydroaluminate $\mathrm{[Li(thf)_2(\mu\text{-}NHPh)_2\{AlH[C(SiMe_3)_3]\}]}$ **7** and the alkyltris(amido)aluminate $\mathrm{[Li(thf)_4][Al(NHPh)_3\{C(SiMe_3)_3\}]}$ **8**.



R = $\mathrm{C(SiMe_3)_3}$, **1**
R = $\mathrm{C(SiMe_2Ph)_3}$, **2**



Scheme 1 (i) HCl; (ii) $\mathrm{Br_2}$ or HBr; (iii) $\mathrm{I_2}$; (iv) tmen; (v) $\mathrm{2PhNH_2}$; (vi) $\mathrm{3PhNH_2}$

Results and Discussion

Treatment of the alkyltrihydroaluminate **1** with an excess of tmen resulted in the displacement of the thf from the co-ordination sphere of the lithium to give the compound **3**, which crystallised from toluene as a colourless air- and moisture-sensitive solid. The structure was shown to comprise discrete $\mathrm{[Li(tmen)_2]^+}$ cations and $\mathrm{[AlH_3\{C(SiMe_3)_3\}]^-}$ anions. It is known that the co-ordinating affinities of thf and tmen for lithium are very similar,[9] so it is likely that the formation of separated, rather than hydride-bridged, ion pairs upon crystallisation is determined by very small differences in energy. We cannot be certain of the nature of the species obtained by dissolving compound **3** in benzene or toluene. There is some evidence that the analogous $\mathrm{[Li(tmen)_2][AlH_4]}$, which also forms separated ion pairs in the solid state, gives hydrido-bridged species in benzene,[10] and there are many further examples in the literature of cases where small changes in donor solvents bring about drastic changes in the structures of the solids that crystallise from solution.

Compound **3** crystallised in a large unit cell with two ion pairs and a molecule of toluene in the asymmetric unit. There was no significant difference between the data from the two molecules (Table 1) but those from the first, containing Li(1)

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Table 1 Selected bond lengths (Å) and angles (°) for the alkyltrihydroaluminate ions in $[Li(thf)_2\{AlH_3[C(SiMe_2Ph)_3]\}]_2$ **2**, $[Li(tmen)_2][AlH_3\{C(SiMe_3)_3\}]$ **3**, and the alkyltrianilidoaluminate ion in $[Li(thf)_4][Al(NHPh)_3\{C(SiMe_3)_3\}]$ **8**

	$[AlH_3\{C(SiMe_2Ph)_3\}]^-$ [a]	$[AlH_3\{C(SiMe_3)_3\}]^-$ [b]	$[Al(NHPh)_3\{C(SiMe_3)_3\}]^-$
Al–C	2.046(4)	2.052(6), 2.066(7)	2.044(4)
Al–X (X = H or N)	1.61(4)	1.55(6), 1.57(6)	1.851(4)
Si–C(1) (mean)	1.887(5)	1.864(6), 1.864(7)	1.878(4)
Si–Me (mean)	1.879(5) [c]	1.882(7), 1.891(7)	1.879(5)
X–Al–X	105(2)	108(3), 107(3)	110.4(2), 108.4(2), 108.9(2)
C–Al–X	114(1)	111(2), 112(2)	106.7(2), 112.0(2), 110.4(2)
Al–C–Si	108.0(2) (mean)	106.7(3), 106.7(3) (mean)	107.1(2), 108.0(2), 111.1(2)
Si–C(1)–Si (mean)	110.9(2)	112.1(3), 112.1(3)	110.2(2)
C(1)–Si–Me (mean)	113.8(2) [c]	113.6(3), 112.9(3)	114.2(2)
Me–Si–Me	104.8(2) [c]	105.0(3), 105.7(4)	104.4(2)

[a] Ref. 1 and unpublished work. [b] Data for two independent molecules. [c] Includes Si–Ph as well as Si–Me.

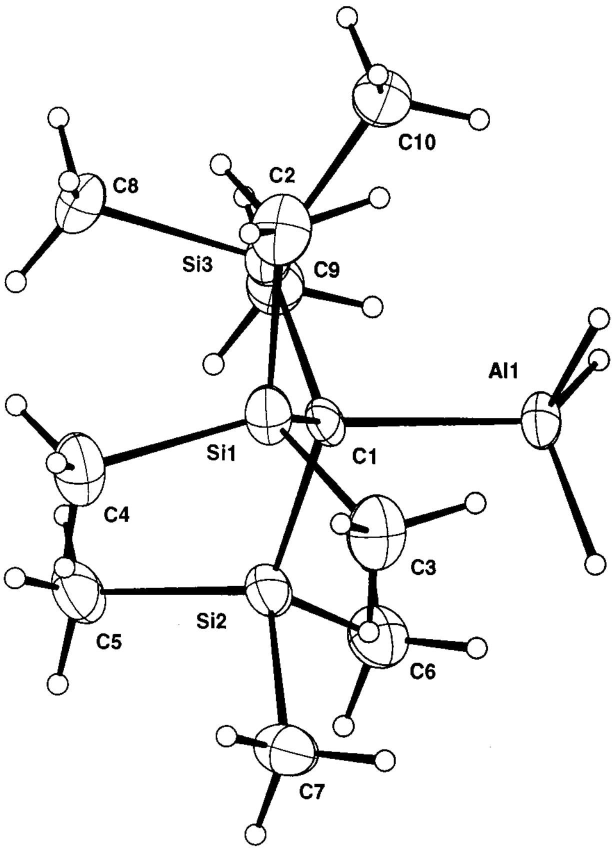

Fig. 1 Structure of the anion $[AlH_3\{C(SiMe_3)_3\}]^-$ of compound **3**

and Al(1), are the more consistent and reliable since the cation containing Li(2) was disordered between two sets of ligand positions with occupancies which refined to 0.81 : 0.19, and in the anion containing Al(2) the Si atoms were disordered between sites with occupancies 0.75 : 0.25. The structure of the anion containing Al(1) in **3** is shown in Fig. 1. There is no significant difference between the principal bond lengths and angles within the anion in the bridged compound **2** and those in the separate ion of **3**, confirming the formulation of **2** as a dimeric ion pair rather than a lithium aluminium hydride complex. The Al–C and Al–H bond lengths in **3** are in the usual range and the mean Si–C(1) and Si–Me bond lengths are similar, as expected from the electronegativity of aluminium.[11]

Table 2 Selected bond lengths (Å) and angles (°) for the alkylaluminium halides $[AlBr_2\{C(SiMe_3)_3\}]\cdot thf$ **5** and $[AlI_2\{C(SiMe_3)_3\}]\cdot thf$ **6**

	X = Br **5**	X = I **6**
Al–X	2.315(2)	2.561(1)
Al–C	1.973(8)	1.980(6)
Al–O	1.881(6)	1.886(4)
Si–C(1) (mean)	1.900(8)	1.905(3)
C–Al–X	116.9(1)	117.8(1)
O–Al–C	114.8(3)	115.7(2)
Al–C–Si	110.5(3)	110.1(2)
	107.3(4)	109.6(2)
	110.0(4)	107.5(3)
Si–C(1)–Si (mean)	109.7(4)	109.9(3)
X–Al–X	105.3(1)	102.6(1)
O–Al–X	100.2(1)	100.0(1)

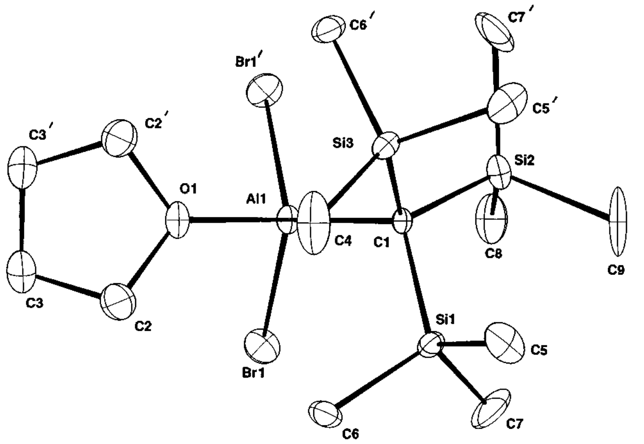

Fig. 2 Molecular structure of $[AlBr_2\{C(SiMe_3)_3\}]\cdot thf$ **5**

Reactions of 1 equivalent of compound **1** with a little more than 3 equivalents of hydrogen halides proceeded smoothly at room temperature to yield the complexes $[AlX_2R]\cdot thf$, X = Cl **4** or Br **5**, without attack on the Al–C bond. Reactions of 1 equivalent of **1** with 3 equivalents of Br_2 or I_2 gave, respectively, **5** or $[AlI_2R]\cdot thf$ **6**, but in lower yield; with Cl_2 a complicated mixture, including RH and RCl, was obtained. The compounds **4**–**6** were characterised by elemental analyses and multinuclear NMR spectroscopy, and in the case of the dibromide **5** and the diiodide **6** by determination of the crystal structures. These two compounds were isostructural; molecules were disordered across a plane of symmetry and those with alternative sets of silicon positions shared overlapping unresolved methyl carbon sites. This type of disorder is common in the structures of compounds containing the $C(SiMe_3)_3$ fragment.[12] The molecular structure of **5** is shown in Fig. 2 (that of **6** is similar so it is not reproduced) and bond lengths and angles for both **5** and **6** are given in Table 2. The lengths of the Al–C and Al–O bonds are similar in the two compounds and similar to those in the arylaluminium compounds $AlBr_2R\cdot OEt_2$ with R = 2,4,6-$Ph_3C_6H_2$ **9** [Al–C 1.983(9), Al–O 1.868(8) Å][6] and R = 2,4,6-$Pr^i{}_3C_6H_2$ **10** [Al–C 1.976(14), Al–O 1.865(11) Å].[13] The Al–Br bond lengths are also in the usual range,[14] *cf.* 2.300(3) Å in **9**, 2.311(6) Å in **10**, 2.313(2) Å in $AlBr_2[C_6H_4(CH_2NMe_2\text{-}2)]$ **11**,[15] and 2.22(2)

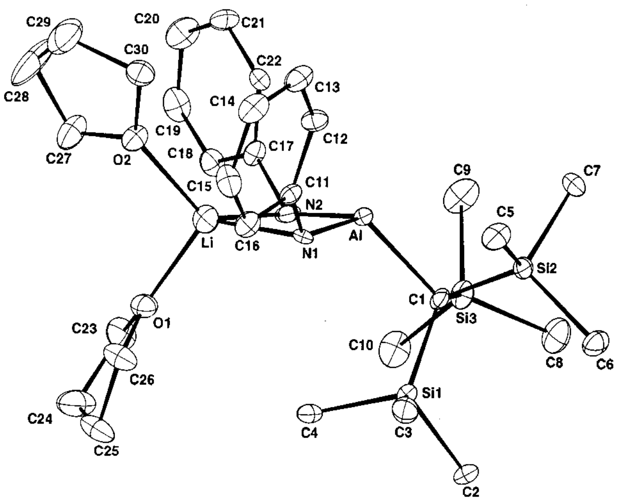

Fig. 3 Molecular structure of $[Li(thf)_2(\mu\text{-}NHPh)_2\{AlH[C(SiMe_3)_3]\}]$ **7**

and 2.41(7) Å for the terminal and bridge bonds in Al_2Br_6.[16] The Br–Al–Br angle is between those in **9** [109.4(1)°] or **11** [108.4(1)°] and that in **10** [103.4(2)°]; in Al_2Br_6 the Br–Al–Br angles range from 93 to 122(2)°. The compound **6** is the first alkylaluminium diiodide to be structurally characterised. The paucity of data on this class of compound may reflect the ready rearrangement to $AlIR_2$ and AlI_3[17] enhanced by the presence of strong bases,[18] a rearrangement prevented by the attachment of bulky groups to aluminium. The Al–I bond length, 2.561(1) Å, is intermediate between those of the terminal (mean 2.453 Å) and bridging bonds (mean 2.720 Å) in the chain structure of solid AlI_3,[19] about the same as that in $AlIMe_2{\cdot}NMe_3$ (2.58 Å)[20] and longer than those in the cage compound $Al_4I_4(SMe)_4S_2$ [2.497(9) Å][21] and the dimers $(AlI_2OSiHMe_2)_2$ **12** [2.470(2) Å] and $(AlI_2NMe_2)_2$ **13**, [2.491(5) Å].[22] The I–Al–I angle is smaller than the Br–Al–Br angle in **5** and significantly below the tetrahedral value, but about the same as that, 102.4°, in $Cs[AlI_2Me_2]{\cdot}C_6H_4Me_2$-*p*.[23] The wider angles in **12** (116.4°) and **13** (110.7°) may result from constraints imposed by the four-membered rings. In AlI_3 the I–Al–I angles range from 98.8 to 119.5°.

The reactions of compound **1** with HCl or HBr, which lead to removal of lithium and formation of organoaluminium dihalides stand in contrast to the reaction of **1** with HF/py, which gives the aluminate $[Li(thf)][AlF_3\{C(SiMe_3)_3\}]$.[3]

When 3 equivalents of aniline were added to 1 of compound **1** the product was the dianilidoaluminate **7**, and the crystals which separated from toluene were found to consist of anilido-bridged ion pairs $[Li(thf)_2(\mu\text{-}NHPh)_2\{AlH[C(SiMe_3)_3]\}]$. In one experiment the solvent was removed from the product mixture, the sticky residue was dissolved in hot heptane–thf and the solution cooled to give colourless crystals. The analysis and NMR spectra of these showed that the product was mainly **7**, but a crystal taken for a structure determination was found to be the trianilidoaluminate $[Li(thf)_4][Al(NHPh)_3\{C(SiMe_3)_3\}]$ **8**. It appears that under the conditions of this experiment a small amount of the compound **7** reacted with the excess of aniline. When a sample of compound **7** was heated under reflux in heptane–thf with 1 equivalent of aniline and the solution was allowed to cool slowly to room temperature crystals of compound **8** were obtained.

The structures of compound **7** and the anion of **8** are given in Figs. 3 and 4, respectively, and the bond lengths and angles are given in Tables 3 and 1. The Al–C, Si–C(1) and Si–Me distances are the same in the two compounds and similar to those in **3**, **5** and **6**. Compound **8** is, as far as we are aware, the first alkyltriamidoaluminate to be structurally characterised. A number of tetraamidoaluminates are known but these have bis(amido) bridges like those in compound **7**.[24,25] The Al–N bond lengths in **8** are greater than those in compounds containing three-coordinate Al [*cf.* 1.82–1.89 Å in $Bu^t{}_2AlNR_2$ (R = 2,4,6-$Me_3C_6H_2$ or $SiPh_3$),[26] 1.79–1.80 in $Al(NPr^i{}_2)_3$[27] or 1.795(4) Å in 2,4,6-$Bu^t{}_3C_6H_2Al(NHPh)_2$][28] but they are similar to those of the terminal bonds in lithium tetraamidoaluminates $[Li(thf)_2]$-$[Al(NMe_2)_4]$ [1.845(4) Å][24] and $[Li(thf)_2][Al(NC_5H_{10})_4]$ [1.828(3) Å, NC_5H_{10} = piperidino].[25] The Al–N and Li–N bridging bond lengths in **7** are similar to those found previously.[24–26] The Li–N bonds appear to be significantly longer than those (2.025 Å) in $Li[AlBu^t{}_2(NHCPh_3)_2]$ in which the lithium is η^2 co-ordinated by phenyl rings instead of by thf.[27] The amido hydrogen atoms were visible on a difference map and the geometry at nitrogen shown to be planar, as in most, but not all, amidoaluminium compounds.[24–28] The planes of the phenyl rings are inclined at 21, 48 and 81° to the N_3 plane, indicating that the ion as a whole has no symmetry and that the NHPh groups twist about Al–N bonds to minimise intraligand repulsion.

In compound **7**, if the configurations of the $C(SiMe_3)_3$ groups and thf are ignored, there is an approximate plane of symmetry through the atoms O(1), O(2), Li and C(1). [The mean plane is at 84° to the mean plane of the LiN(1)AlN(2) ring.] There is very flattened tetrahedral geometry at Al (N–Al–C 113°) and N (Al–N–C 132°). The structure of **7** may be compared with that of $LiAlH(NEt_2)_3$ **14**,[29] which has an amido instead of an alkyl group attached to aluminium. The Al–N and Li–N distances in the two compounds are similar but in **14** the lithium is co-ordinated by two NEt_2 groups to give a

Table 3 Selected bond lengths (Å) and angles (°) for $[Li(thf)_2$-$(\mu\text{-}NHPh)_2\{AlH[C(SiMe_3)_3]\}]$ **7**

Al–N(1)	1.888(8)	Al–N(2)	1.871(10)
Al–C(1)	2.022(9)	Al···Li	2.84(2)
O(1)–Li	1.91(2)	O(2)–Li	1.94
N(1)–Li	2.14(2)	N(2)–Li	2.17(2)
Si–C (mean)	1.875(10)	Si–Me (mean)	1.871(10)
N(2)–Al–N(1)	98.1(4)	N(2)–Al–C(1)	113.0(4)
N(1)–Al–C(1)	113.6(4)	O(1)–Li–O(2)	104.3(9)
O(1)–Li–N(1)	117.3(9)	O(2)–Li–N(1)	120.7(9)
O(1)–Li–N(2)	106.8(8)	O(2)–Li–N(2)	124.5(9)
N(1)–Li–N(2)	82.5(7)	Me–Si–Me (mean)	105.1(6)
Si–C–Si (mean)	111.2(5)	C–Si–Me (mean)	113.5(5)

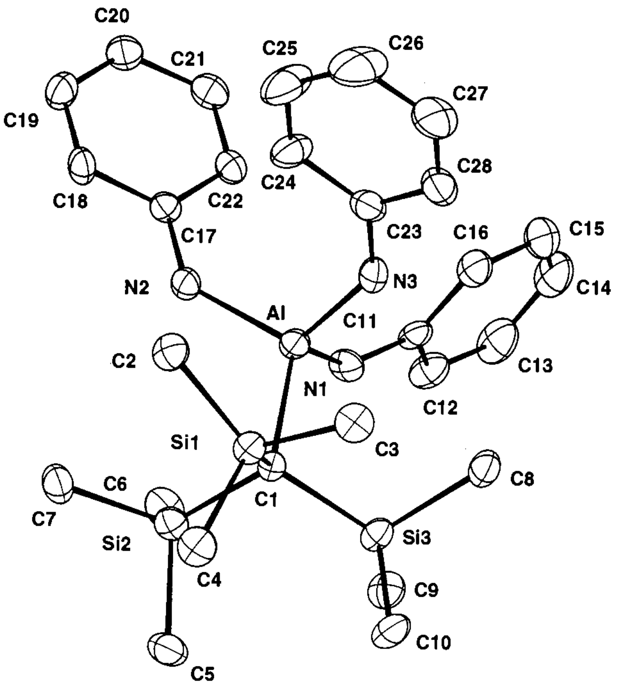

Fig. 4 Structure of the anion $[Al(NHPh)_3\{C(SiMe_3)_3\}]^-$ of compound **8**

Table 4 Crystal data and structure determinations for compounds **3** and **5**–**8**

	3	**5**	**6**	**7**	**8**
Empirical formula	$C_{22}H_{62}AlLiN_4Si_3 \cdot 0.5C_7H_8$	$C_{14}H_{35}AlBr_2OSi_3$	$C_{14}H_{35}AlI_2OSi_3$	$C_{30}H_{56}AlLiN_2O_2Si_3$	$C_{44}H_{77}AlLiN_3O_4Si_3$
Formula weight	547.0	490.5	584.5	595.0	830.3
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic
Space group	*C*2/*c*	*Pbcm*	*Pbcm*	$P2_12_12_1$	$P2_1/n$
a/Å	17.315(7)	12.558(4)	12.506(7)	9.549(3)	16.087(5)
b/Å	26.471(9)	13.394(4)	13.946(3)	16.885(5)	16.907(6)
c/Å	32.800(13)	13.434(6)	13.755(3)	21.913(4)	18.360(11)
β/°	91.16(3)				98.59(4)
U/Å^3	15 031(10)	2260(1)	2399(2)	3533(2)	4938(4)
Z	16	4	4	4	4
D_c/Mg m^{-3}	0.97	1.44	1.62	1.12	1.12
μ/mm^{-1}	0.17	3.78	2.81	0.19	0.15
F(000)	4880	1008	1152	1296	1808
Crystal size/mm	0.3 × 0.3 × 0.2	0.4 × 0.3 × 0.3	0.4 × 0.4 × 0.1	0.35 × 0.25 × 0.15	0.4 × 0.4 × 0.3
θ Range/°	2–22	2–28	2–25	2–25	2–25
hkl Ranges	0–18, 0–27, −34 to +34	0–16, 0–17, 0–17	0–14, 0–16, 0–16	0–11, 0–20, 0–26	0–19, 0–20, −21 to +21
Reflections collected	9558	2827	2208	3494	8985
Independent reflections	9206	2827	2208	3494	8666
Reflections with $I > 2\sigma(I)$	4951	1408	1792	2221	4799
Data/restraints/parameters	9206/0/742	2826/0/118	2208/0/118	3494/0/361	8666/0/505
Goodness of fit on F^2	1.02	1.04	1.06	1.03	1.02
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.079, 0.178	0.065, 0.102	0.030, 0.076	0.080, 0.192	0.074, 0.153
(all data)	0.157, 0.224	0.162, 0.134	0.044, 0.082	0.134, 0.227	0.145, 0.192

polymeric chain $\{Li(\mu\text{-}H)(\mu\text{-}NEt_2)Al(\mu\text{-}NEt_2)_2\}_n$ and the Li · · · Al bridge is made by one hydrogen and one amido group. The ability of hydrogen atoms attached to aluminium to compete with amine or ether donors for places in the co-ordination sphere of lithium has been demonstrated in the compounds $(NC_5H_8Me_2)_2Al(\mu\text{-}H)_2Al(NC_5H_8Me_2)_2$ ($NC_5H_8Me_2$ = 2,6-dimethylpiperidino)[30] and $[\{Li(tmen)(AlH_4)\}_2]$.[10] Of the presently characterised compounds $LiL_m[AlH_{3-n}R(NHPh)_n]$, [R = $C(SiMe_3)_3$], those with $n = 0$ show both bridged and solvent-separated forms. The compound with $n = 2$ has a $(\mu\text{-}NHPh_2)_2$ bridged structure with terminal Al–H bonds and that with $n = 3$ has a solvent separated structure with discrete $[Li(thf)_4]^+$ cations and $[AlR(NHPh)_3]^-$ anions in the crystal lattice.

Experimental

Air and moisture were excluded as far as possible from all reactions by use of standard Schlenk techniques and Ar as blanket gas. Solvents were dried by normal procedures and distilled immediately before use. The IR spectra were for Nujol mulls, NMR spectra were recorded, on samples dissolved in C_6D_6, at 300.13 (^1H), 75.43 (^{13}C), 97.26 (^7Li), 65.22 (^{27}Al) and 99.4 (^{29}Si) MHz. Chemical shifts are relative to $SiMe_4$ for H, C, and Si, and aqueous LiCl or $Al(NO_3)_3$ for Li and Al, respectively. Molar quantities of compound **1** are for monomer.

Syntheses

$[Li(tmen)_2][AlH_3\{C(SiMe_3)_3\}] \cdot 0.5C_6H_5Me$ 3. An excess of tmen (0.30 cm^3, 2.00 mmol) was added to a solution of compound **1** (0.40 g, 0.97 mmol) in toluene (20 cm^3) and the mixture stirred at room temperature for 20 h. It was then filtered through Celite, about half of the solvent was removed from the filtrate and colourless air- and moisture-sensitive crystals of **3** separated at −30 °C. Yield 0.36 g (75%), m.p. 138 °C (satisfactory C, H, N analyses were not obtained). $\tilde{\nu}_{max}$/cm^{-1} 1705 (sh) and 1635s; δ_H 0.65 (27 H, s, Me_3Si), 1.94 (24 H, s, tmen) and 1.96 (8 H, s, tmen); δ_C 5.2 (Me_3Si), 46.0 and 57.7 (tmen); δ_{Li} 0.15; δ_{Al} 115, $\Delta\nu_{\frac{1}{2}}$ 400 Hz; δ_{Si} −1.7.

$[AlCl_2\{C(SiMe_3)_3\}] \cdot thf$ 4. Hydrogen chloride gas (4.52 mmol) was condensed on to a frozen solution of compound **1** (0.565 g, 1.37 mmol) in toluene (20 cm^3) at 77 K. The mixture was allowed to warm to room temperature and stirred for 16 h. The white solid was filtered off, and the filtrate concentrated then kept at −30 °C overnight to give colourless moisture-sensitive crystals of **4** (0.28 g, 51%), m.p. 210 °C (Found: C, 41.8; H, 8.7. $C_{14}H_{35}AlCl_2OSi_3$ requires C, 41.9; H, 8.8%); $\tilde{\nu}_{max}$/cm^{-1} 1263 (sh) 1254s, 988m, 921w, 853s, 835 (sh), 798 (sh), 752w and 672m; δ_H 0.45 (27 H, s, $SiMe_3$), 0.91 and 3.92 (thf); δ_C 6.0 ($SiMe_3$), 24.2 and 75.3 (thf); δ_{Al} 123, $\Delta\tilde{\nu}_{\frac{1}{2}}$ 1.96 kHz; δ_{Si} −3.4; *m*/*z* 313 (40, *M* − thf − Me), 237 (65) and 201 (100). There were also weak peaks at *m*/*z* 657 (2*M* − 2thf), 583 (2*M* − 2thf − $SiMe_3$) and 509.

$[AlBr_2\{C(SiMe_3)_3\}] \cdot thf$ 5. Liquid Br_2 (0.17 g, 1.06 mmol) was added dropwise to a stirred solution of compound **1** (0.26 g, 0.63 mmol) in toluene (25 cm^3) at 0 °C. The mixture was stirred at room temperature for 24 h during which a white solid separated. This was filtered off and the filtrate concentrated then kept at −30 °C overnight to give large colourless cubes of **5** (0.11 g, 35%), m.p. 217 °C (Found: C, 33.7; H, 7.1. $C_{14}H_{35}AlBr_2OSi_3$ requires C, 34.3; H, 7.2%); $\tilde{\nu}_{max}$/cm^{-1} 1290w, 1253s, 1171w, 1048w, 985m, 920m, 852s, 803 (sh) and 667w. δ_H 0.47 (27 H, s, $SiMe_3$), 0.94 and 3.99 (thf); δ_C 6.2 ($SiMe_3$), 24.1 and 76.1 (thf); δ_{Al} 113, $\Delta\nu_{\frac{1}{2}}$ 1.96 kHz; δ_{Si} −3.4; *m*/*z* 475 (10, *M* − Me), 403 (40, *M* − Me − thf) and 201 (95). Compound **5** was also made in 49% yield from the reaction of **1** with HBr.

$[AlI_2\{C(SiMe_3)_3\}] \cdot thf$ 6. Solid iodine (0.24 g, 0.95 mmol) was slowly added to a stirred solution of compound **1** (0.24 g, 0.58 mmol) in toluene (20 cm^3) at 0 °C. The mixture was stirred for 18 h at room temperature and the white solid then filtered off. The filtrate was concentrated then kept at −30 °C overnight to give colourless crystals of **6** (0.06 g, 18%), m.p. 294 °C (Found: C, 29.0; H, 6.0. $C_{14}H_{35}AlI_2OSi_3$ requires C, 28.7; H, 6.0%). $\tilde{\nu}_{max}$/cm^{-1} 1289m, 1260s, 1232 (sh), 978w and 854s; δ_H 0.50 (27 H, s, $SiMe_3$), 0.94 and 4.09 (4 H, thf); δ_C 6.6 ($SiMe_3$), 24.0 and 77.2 (thf); δ_{Al} 92, $\Delta\nu_{\frac{1}{2}}$ 2.62 kHz; δ_{Si} −3.2; *m*/*z* 569 (20, *M* − Me), 497 (95, *M* − Me − thf) and 385 (100, *M* − I − thf).

$[Li(thf)_2(\mu\text{-}NHPh)_2\{AlH[C(SiMe_3)_3]\}]$ 7. Aniline (0.62 cm^3, 6.78 mmol) was added dropwise to stirred solution of compound **1** (0.93 g, 2.26 mmol) in toluene (25 cm^3) at room temperature. Dihydrogen was immediately evolved. The mixture was stirred overnight then filtered and solvent removed in vacuum from the filtrate until crystals appeared. These were dissolved by gentle warming and the solution kept at room temperature to give colourless needles of compound **7** (0.90 g, 67%), m.p. 164 °C (Found: C, 59.2; H, 9.45; N, 4.7. $C_{30}H_{56}AlLiN_2O_2Si_3$ requires C, 60.6; H, 9.5; N, 4.7%). $\tilde{\nu}_{max}/cm^{-1}$ (Al–H) 1795; δ_H 0.46 (27 H, s, $SiMe_3$), 2.83 (2 H, br s, NH), 1.1 and 3.08 (8 H, thf) and 6.7–7.2 (10 H, m, Ph); $\delta_H\{^{27}Al\}$ 5.1 (Al–H); δ_C 5.7 ($SiMe_3$), 25 and 68 (thf), 116 (*o*-C), 118 (*p*-C), 128 (*m*-C) and 153 (*ipso*-C); δ_{Li} −0.09; δ_{Al} 129.5, $\Delta\nu_{\frac{1}{2}}$ 1.6 kHz; δ_{Si} −4.04.

[Li(thf)$_4$][Al(NHPh)$_3${C(SiMe$_3$)$_3$}] 8. In an experiment like that described in the previous paragraph, solvent was removed from the product mixture obtained from aniline (0.39 cm^3, 4.28 mmol) and compound **1** (0.59 g, 1.43 mmol) in toluene (15 cm^3). The sticky white solid was dissolved in hot heptane–thf (9 : 1) and colourless air-sensitive crystals which were judged from microanalysis and NMR spectroscopy to be compound **7** separated. However a crystal selected for a structure determination proved to be of compound **8**. In another experiment a mixture of aniline (0.084 mmol) and **7** (0.084 mmol) was heated in heptane–thf. The colourless crystals obtained when the solution was cooled slowly gave an NMR spectrum which showed peaks for Me_3Si, thf and NH in the ratio 27 : 32 : 3 as required for **8**, and no peak in the ν(Al–H) region of the IR spectrum. The solid was not investigated further.

Crystallography

Data were collected at 173(2) K on a CAD4 diffractometer by use of Mo-Kα radiation (λ = 0.71073 Å). Further details are described in Table 4. In compound **3** most non-hydrogen atoms were anisotropic but those in the low-occupancy tmen sites were left isotropic and their H atoms were omitted. Other H atoms were included in the riding mode with $U_{iso} = 1.2U_{eq}(C)$ or $1.5U_{eq}(C)$ for methyl groups. Hydrogen atoms attached to Al were located on a difference map and freely refined. In compounds **5**–**8** all non-hydrogen atoms were anisotropic and H atoms were included in the riding mode with $U_{iso} = 1.2U_{eq}(C)$ or $1.5U_{eq}(C)$ for methyl groups.

CCDC reference number 186/1015.

See http://www.rsc.org/suppdata/dt/1998/2411/ for crystallographic files in .cif format.

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